

Persistent Organic Pollutants in the Environment: Chlordane Residues in Compost

Wen-Yee Lee, William Iannucci-Berger, Brian D. Eitzer, Jason C. White, and MaryJane Incorvia Mattina*

ABSTRACT

The half-lives of some persistent organic pollutants (POPs) in environmental compartments such as soil and air can be as long as decades. In spite of the hydrophobicity of many POPs, the literature contains reports of their uptake by, and translocation through, a variety of plants. Both these observations prompt the investigation of whether a vegetation-based environmental compartment such as compost contains significant residues of POPs. Previous reports imply that residues of technical chlordane will be found in compost. Due to its physicochemical properties, technical chlordane provides insights into the fate of POPs in the environment, which are not accessible through determinations of other pollutants in this group. Accordingly, we undertook the first comprehensive examination of technical chlordane residues in a variety of composts, specifically, 13 commercial and 39 municipal compost products, to both characterize and quantify the magnitude of this point source of contamination. Using chiral gas chromatography interfaced to ion trap mass spectrometry, the concentration and the compositional and enantiomeric profiles of chlordane components were determined. Of the 13 commercial products, 9 contained detectable chlordane concentrations, ranging from 4.7 to 292 $\mu\text{g/kg}$ (dry wt.), while all 39 municipal products contained chlordane residues ranging from 13.9 to 415 $\mu\text{g/kg}$ (dry wt.). The residue concentrations and profiles suggest possible feedstock sources for the chlordane in the finished compost product. The data also support the conclusion that some composts contribute to anthropogenic cycling of POPs through the biosphere.

PERSISTENT ORGANIC POLLUTANTS are a group of chemicals that include dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), heptachlor, dioxins, toxaphene, and technical chlordane. Although some POPs are naturally occurring—the polyaromatic hydrocarbons (PAHs), for example—most are synthetic organochlorines introduced anthropogenically into the environment as industrial chemicals, agrochemicals, or unintentional byproducts of industrial processes. As the name implies, POPs are characterized by long half-lives in the environment; technical chlordane, for instance, has a half-life in soil that exceeds twenty years (Incorvia Mattina et al., 1999). The long-term persistence of POPs, coupled with their lipophilicity, contribute to the reported bioaccumulation and biomagnification through faunal-based food chains (Jones and de Voogt, 1999; Wiberg et al., 2000).

After anthropogenic introduction of POPs into the environment, physicochemical properties of the chemicals generally control their dispersal, primarily via atmospheric transport, through the biosphere. It is reasonable, therefore, that most studies to date regarding the cycling

of POPs through the environment have focused on non-point sources as reservoirs of the contaminants, for example, volatilization of POPs from soils and water, translocation of POPs through the atmosphere to produce the “grasshopper effect” (Bidleman and Falconer, 1999), and their accumulation in food products such as fish and milk (Iwata et al., 1993).

As POPs in soil weather over the decades, it is noted that they become less accessible to extraction by organic solvents, microbial degradation, and uptake by organisms such as earthworms (Kelsey and Alexander, 1997; Alexander, 2000). Further, many of the POPs are organochlorine compounds whose hydrophobicity is indicated by log K_{OW} values that exceed 3. For such compounds it is assumed that uptake into and movement through the aqueous transport system of plants will be minimal (Schnoor et al., 1995). In spite of both these issues, research from this laboratory has shown that a wide variety of plants can uptake weathered soil residues of POPs such as chlordane and DDE within a single growing season (Incorvia Mattina et al., 2000; White, 2001) and transport the compounds through the aerial plant tissue. Therefore, it is possible that POPs can be transferred via contaminated plant materials to compost feedstock. Due to their considerable thermal stability, POPs may be expected to survive the composting process and remain in the finished product for transport to noncontaminated sites. These observations make it appropriate to determine the significance that compost, a potential point source of contamination, plays on total POPs cycling through the environment.

Technical chlordane was introduced commercially in the 1940s and used in the United States until 1988 when the USEPA banned all uses as well as its sale (Dearth and Hites, 1991). It is listed as one of the 12 POPs subject to global treaty restrictions (Hogue, 2001). It was chosen as the representative POP in this study for several reasons. First, it has been detected previously in a limited number of compost samples (Büyüksönmez et al., 2000; Strom, 2000). Second, technical chlordane was an agrochemical used in both agricultural and residential applications in substantial quantities, and is, therefore, expected to be a common weathered soil residue available for plant uptake and subsequent transfer to compost feedstock. The technical product applied was not a single chemical; detailed analysis shows that it consists of 147 distinct components (Dearth and Hites, 1991). Of these 147 components several contain centers of optical activity and, therefore, are chiral, including two of the three major components, *trans*-chlordane (TC) and *cis*-chlordane (CC). The third major component in the technical mixture, *trans*-nonachlor (TN), is

W.-Y. Lee, W. Iannucci-Berger, B.D. Eitzer, and M. Incorvia Mattina, Dep. of Analytical Chemistry, and J.C. White, Dep. of Soil and Water, Connecticut Agricultural Experiment Station, 123 Huntington Street, New Haven, CT 06511. Received 29 Mar. 2002. *Corresponding author (MaryJane.Mattina@po.state.ct.us).

Abbreviations: CC, *cis*-chlordane; EF, enantiomer fraction; POP, persistent organic pollutant; TC, *trans*-chlordane; TN, *trans*-nonachlor.

achiral. Not only are these three components the most abundant, but they persist through decades of weathering (Incorvia Mattina et al., 1999). Changes in the abundance ratios of the three components from those in the technical mixture to those in weathered residues are largely, although not exclusively, attributed to differences in their physicochemical properties, for example, volatility, and provide insight into the fate of this POP under abiotic influences. However, under biotic influences the two enantiomers of a chiral pair are expected to be affected differentially. Since all chiral components are racemic at their initial introduction into the environment, chiral analysis of weathered chlordane residues can provide information regarding the fate of POPs under biotic influences as well. This is the third justification for choosing technical chlordane as the representative POP residue in compost.

Surveys of pesticides (Strom, 2000) and heavy metals (Stilwell, 1993) in compost have been reported. Although chlordane has been detected, none of the prior studies has addressed the chirality of the chlordane residues in compost, or the relative abundances of the individual chlordane components. Since the effect of POPs on human health cannot be assessed fully without understanding the cycling of POPs through both biotic and abiotic processes, we report here details of the enantiomeric, as well as the compositional, profiles of chlordane components in compost. Specifically, we examined 13 commercial and 39 municipal compost products for several parameters: total chlordane concentration, the compositional profile of the chlordane residues, and the enantiomeric profile of seven chlordane components. The seven components were the enantiomers of TC and CC; achiral TN; and the enantiomers of a chiral, minor, but persistent component of the technical mixture known as MC-5.

MATERIALS AND METHODS

Sample Collection and Preparation

Nationally distributed, commercial compost products were purchased from garden supply stores in Connecticut. Municipal composts were collected from facilities throughout the state, most of which have an annual capacity of at least 8000 yd³ (6117 m³) of uncomposted leaves. Based on recommended sampling techniques (Kratochvil and Taylor, 1981), a 1-kg sample was collected from the top-30-cm layer throughout the pile, composited, and stored in clean, tightly capped amber glass jars with Teflon-lined caps at room temperature. All samples were analyzed within two months of collection.

Each compost sample was thoroughly mixed to ensure homogeneity, removing large, nonvegetative debris while mixing. For each sample two 10-g subsamples were extracted for chlordane analysis; a third 10-g subsample of each compost sample was weighed in an aluminum weigh boat and dried in an oven at 105°C overnight to ascertain the moisture content. The same subsample was further used to determine organic content by ashing at 550°C for at least 6 h.

Extraction and Cleanup

The extraction procedure developed for compost is similar to that previously employed for vegetation (Incorvia Mattina

et al., 2000) with some modifications. Each 10-g subsample was transferred into a blender jar and spiked with 25 μ L of internal standard solution containing 4 mg/L racemic ¹³C₁₀ TC + 2 mg/L ¹³C₁₀ TN (Cambridge Isotope Laboratories, Andover, MA) in toluene. To the blender jar were added 10 mL of distilled water, 25 mL of 2-propanol, and 50 mL of petroleum ether, followed by blending of the mixture for five minutes. The addition of water improved the extraction efficiency (Lee, unpublished data, 2001). The blended mixture was filtered through glass wool into a separatory funnel, to which was added 100 mL distilled water and 10 mL of saturated sodium sulfate solution. After mixing, the contents were allowed to settle and the lower water layer was discarded. The organic layer was dried over sodium sulfate and cleaned on a Florisil (U.S. Silica, Berkeley Springs, WV) PR grade 60/100 mesh (Incorvia Mattina et al., 2002). The extract was concentrated and solvent exchanged to a final volume of 1 mL in iso-octane for analysis by chiral gas chromatography with ion trap mass spectrometric detection.

Analysis and Quantitation

Extracts were analyzed on a Saturn 2000 Ion Trap gas chromatography-mass spectrometry (GC-MS) system (Varian, Sugar Land, TX) equipped with a 30-m length \times 0.25-mm i.d. \times 0.25- μ m film thickness γ -DEX-120 column (Supelco, Bellefonte, PA). A deactivated silica guard column (0.5 m \times 0.25 mm) was attached before and after the analytical column with press-tight connectors (Restek, Bellefonte, PA). The GC oven was programmed as follows: initial temperature 120°C, hold 1 min; ramped at 20°C/min to 155°C; ramped at 0.5°C/min to 195°C; ramped at 20°C/min to 230°C, hold for 21.6 min. The injection port was maintained at 230°C, and a 3- μ L splitless injection was used. The mass spectrometer conditions were: a 38-min filament delay, emission current 60 μ A, target total ion current 5000 counts, maximum ionization time 25 000 μ s, multiplier offset +200 V, and scan range m/z 345 to 425.

A set of calibration standards containing TC, CC, and TN were prepared in iso-octane at the following levels: 10, 25, 50, 100, 250, 500, and 1000 μ g/L. Each solution contained racemic TC and CC at the cited concentration, and TN at one-half the cited amount. The calibration solutions also contained oxychlordane (OXY), but since only 6 out of 52 samples contained this metabolite, all at concentrations below 4.7 μ g/kg, it was not considered further in this study. Every calibration solution contained 50 μ g/L of each labeled component: (+)-¹³C₁₀-TC, (–)-¹³C₁₀-TC, and ¹³C₁₀-TN. For each instrumental run of 10 to 20 samples, a complete set of standards was injected twice, once before and once after injection of the set of sample extracts. A single injection of each sample extract was made. Since the chiral column is rapidly fouled by injections of the compost extract, iso-octane was injected between all compost sample injections to control the spectrum noise level and to prolong column lifetimes.

Data reduction, quality assurance and control, and limits of quantitation were developed and described in detail previously (Eitzer et al., 2001; White et al., 2002). Briefly, each compost sample was extracted in duplicate. Should the standard deviation of the average between the two extractions of a single sample exceed 20%, a third extraction was performed. Laboratory solvent blanks were used to test for laboratory contamination. Since all quantitations were performed by internal standard calibration, loss of native analyte through the extraction and cleanup steps was compensated for, providing an accurate value of the native chlordane components initially extracted from the sample. All component peaks were required to have a signal to noise ratio equal to or greater than

2 to 1 in the original chromatogram to exceed the limit of detection (LOD). The limit of quantitation (LOQ) for the analysis was set to meet the following criteria: sample area counts were required to be within the range bounded by 2σ (standard deviation) below the average area of the lowest concentration standard to 2σ above the average area of the highest concentration standard analyzed in the same instrumental run. Principal component analysis (PCA) was performed with SYSTAT and other statistical analyses with SIGMASTAT (SPSS, 2000).

RESULTS AND DISCUSSION

Total Chlordane Concentration

The 13 commercial products and 39 municipal compost samples were each classified into categories based either on ingredient information on the product package (for commercial samples) or feedstock information obtained from personnel at the composting sites (for municipal samples) (Table 1).

Eight chlordane components were determined in each sample: (\pm)-*trans*-chlordane (TC), (\pm)-*cis*-chlordane (CC), (\pm)-MC-5, *trans*-nonachlor (TN), the only achiral component analyzed in this study, and oxychlordane (OXY). The concentrations of seven chlordane components in all the compost samples are reported in Table 1. All concentration values are expressed on a dry weight basis. Because standards were not available, MC-5a and MC-5b were used for labeling the two enantiomers of MC-5 (Incorvia Mattina et al., 2002) and the quantitation of MC-5 enantiomers was based on the average response factor from (+)-TC, (-)-TC, (+)-CC, and (-)-CC. The concentrations of MC-5a and MC-5b ranged from below the detection level to 21.5 $\mu\text{g/kg}$ and from below detection level to 24.3 $\mu\text{g/kg}$, respectively. Twenty out of fifty-two samples had concentrations of MC-5a and MC-5b either below the limit of detection or below the limit of quantitation; therefore, the total chlordane concentration is presented as the sum of concentrations of only five chlordane components, (+)-TC, (-)-TC, (+)-CC, (-)-CC, and TN. We have previously presented arguments supporting the use of this sum as representative of the technical chlordane residue in the weathered environmental compartment under examination (Incorvia Mattina et al., 1999). For the sake of completeness of the data set, MC-5 concentrations have been included in Table 1.

Moisture and organic content were determined for all samples. Moisture content ranged from 11 to 71% and organic content from 4 to 65%. Higher moisture content was often associated with higher organic content, an observation for both compost and soil (Maynard, 1994; Brady and Weil, 1999, p. 19). No association was found, however, between total chlordane concentration and either moisture or organic content.

Chlordane residues were found in 9 out of 13 commercial products and in all municipal composts. Total chlordane concentration ranged from below detection level to 291.8 $\mu\text{g/kg}$ with an average of 49.5 ± 81.4 $\mu\text{g/kg}$ (σ) in commercial products; in municipal composts the range was 13.9 to 415.4 $\mu\text{g/kg}$ with an average of $111.7 \pm$

90.6 $\mu\text{g/kg}$ (σ). Chlordane residues in the 33 leaf composts (L in Table 1) from the current study are compared with other published reports and summarized in Table 2. Data from the present study are at the low end of the range of concentrations in the summary provided in Table 2, but since analytical details such as the definition of total chlordane concentration are minimal in the previous reports, this comparison is not rigorously quantitative.

Figure 1 presents the total chlordane concentration distribution by compost category for all samples analyzed in the present study. It is evident from this histogram that all samples in the "municipal leaf" category (L) contain chlordane residues and these residues are in the higher concentration ranges. Samples in the TS (comm), C + TS, TS(muni), and L + TS categories, on the other hand, have lower total chlordane concentrations, ranging from below detection limit to 69.7 $\mu\text{g/kg}$. Furthermore, it is interesting to note in the data in Table 1 that the total chlordane concentration in MUN2-c (TS) was substantially lower than that in MUN2-a (L) and that the total chlordane concentration in MUN2-b (L + TS) was lower than MUN2-a (L) but higher than MUN2-c (TS). Similar trends were observed in the MUN7, MUN11, MUN12, and MUN13 sample groups. Strom (Strom, 2000) has suggested that "... the residential soil incorporated with leaves and grass clippings during collection ..." was the likely source of observed chlordane in New Jersey compost since "chlordane is not expected to be taken up by plant roots, nor translocated into the tree or grass leaves." While it is premature to use the data from the present study to identify the chlordane-contaminated feedstock, additional data support the conclusion that soil is probably not the sole source of chlordane residues in compost. Several additional pieces of data support this conclusion. First, leaf samples were collected at various times during 2001 and analyzed for chlordane, and the data are summarized in Table 3. The data show that leaves collected at the end of a growing season contain measurable levels of chlordane residues, without establishing explicitly if leaf contamination occurs via a soil-to-plant or an air-to-plant route. Second, we have also analyzed grass clippings and the common lawn weed, dandelion, growing in chlordane-contaminated soil in May 1999 on the campus of the Connecticut Agricultural Experiment Station; 326 and 700 $\mu\text{g/kg}$ (dry wt.) of total chlordane were found in these two vegetation forms, respectively. Although limited in scope, the data establish that vegetation such as leaves and grass clippings do contain and, therefore, contribute chlordane to the finished commercial and municipal compost products. Other researchers have suggested that vegetation such as fruits and vegetables may be the sources of chlordane and other chlorinated pesticides detected in three household-produced composts (Wågman et al., 1999). Additional studies are warranted to establish unequivocally the relative contributions from various feedstocks of chlordane to municipal compost, as well as the uptake pathway of contamination of the feedstock.

The data from this study may be variously employed

Table 1. Chlordane residues in commercial and municipal composts.

Sample code [†]	Label	Category [‡]	(+)-TC [§]	(-)-TC	(-)-CC [§]	(+)-CC	MC-5a [§]	MC-5b	TN [§]	Total
CP1	topsoil	TS (comm)	ND [¶]	ND	ND	ND	ND	ND	ND	ND
CP2	organic compost mix	C + TS	12.2 ± 0.2	13.8 ± 1.5	13.5 ± 1.5	14.3 ± 0.4	ND	ND	15.9 ± 1.6	69.7 ± 4.4
CP3	organic planting mix	C + TS	ND	ND	ND	ND	ND	ND	ND	ND
CP4-a	topsoil	TS (comm)	0.8#	0.9#	0.8#	1.2#	ND	ND	1.1#	4.7
CP4-b	topsoil	C + TS	ND	ND	ND	ND	ND	ND	ND	ND
CP4-c	composted manure + organic humus	C	0.8#	1.0#	0.9#	1.3#	ND	ND	1.4#	5.4
CP5-a	dehydrated manure plus organic humus	C	1.1#	1.5#	1.5#	1.6#	0.5#	0.5#	2.1#	7.8
CP5-b	rich, dark topsoil	C + TS	5.9 ± 0.3	6.4 ± 0.0	7.3 ± 0.0	7.9 ± 0.6	1.8#	2.0#	9.1 ± 0.5	36.6 ± 0.5
CP5-c	organic humus	C	8.1 ± 0.2	8.2 ± 0.4	9.9 ± 0.3	10.7 ± 0.3	1.9#	2.6#	11.3 ± 2.8	48.2 ± 3.9
CP6-a	all-purpose potting soil	C	46.0 ± 4.4	50.8 ± 4.0	56.2 ± 3.0	63.8 ± 6.5	16.2 ± 1.7	17.1 ± 1.4	75.0 ± 6.9	291.8 ± 21.4
CP6-b	all-purpose potting soil	C	19.8 ± 3.3	20.5 ± 2.4	22.4 ± 2.0	26.0 ± 5.0	6.5 ± 0.9	6.1 ± 0.7	28.0 ± 1.4	116.7 ± 14.1
CP6-c	premium planting soil	C	10.5 ± 0.4	12.6 ± 0.6	12.4 ± 0.9	12.4 ± 0.9	2.7 ± 0.1	2.8 ± 0.3	15.2 ± 1.1	63.2 ± 1.8
CP7	potting soil	TS (comm)	ND	ND	ND	ND	ND	ND	ND	ND
Verbal description										
MUN1	leaf compost (1998, 1999)	L	22.7 ± 0.3	22.2 ± 1.2	25.2 ± 1.3	29.6 ± 1.0	ND	ND	51.9 ± 11.5	151.6 ± 10.4
MUN2-a	leaf compost (2000)	L	16.4 ± 1.8	18.0 ± 2.2	19.6 ± 1.5	25.0 ± 4.5	5.5 ± 0.2	6.1 ± 1.7	36.6 ± 10.0	115.6 ± 20.1
MUN2-b	topsoil + 30% leaf compost (2000)	L + TS	5.2 ± 0.0	5.9 ± 0.3	6.8 ± 0.3	8.0 ± 0.0	1.6#	1.7#	9.9 ± 0.8	35.8 ± 1.3
MUN2-c	topsoil	TS (muni)	4.7 ± 0.3	5.4 ± 0.6	5.9 ± 0.6	7.6 ± 0.3	1.4#	1.7#	7.1 ± 0.6	30.5 ± 2.4
MUN3-a	leaf compost (1999, unscreened)	L	17.2 ± 0.1	17.6 ± 0.3	21.3 ± 0.2	22.7 ± 0.1	3.5 ± 2.5	3.5 ± 2.5	26.2 ± 0.1	105.0 ± 0.5
MUN3-b	leaf compost (1999, unscreened)	L	25.3 ± 7.5	26.6 ± 5.7	28.4 ± 3.8	36.5 ± 3.3	6.3 ± 0.9	6.5 ± 0.2	37.8 ± 12.7	154.5 ± 43.0
MUN4	leaf compost (1999, unscreened)	L	12.9 ± 0.7	13.6 ± 0.5	17.1 ± 0.9	20.0 ± 2.0	3.6 ± 0.4	4.9 ± 0.2	25.4 ± 4.3	89.0 ± 5.7
MUN5-a	leaf compost (1998, unscreened)	L	2.6 ± 0.2	2.9 ± 0.1	3.5 ± 0.3	4.1 ± 0.7	1.1#	1.1#	8.0 ± 0.4	21.2 ± 1.7
MUN5-b	leaf compost (1999, unscreened)	L	8.6 ± 0.4	10.5 ± 0.0	12.8 ± 0.2	15.6 ± 0.0	3.4 ± 0.3	4.3 ± 0.5	21.1 ± 1.1	68.6 ± 0.5
MUN5-c	leaf compost (1997, unscreened)	L	8.3 ± 3.0	10.2 ± 1.9	12.5 ± 2.0	15.8 ± 4.9	3.4 ± 1.5	3.8 ± 1.2	28.4 ± 3.7	75.4 ± 15.6
MUN6-a	leaf compost (2000)	L	20.4 ± 0.6	21.4 ± 0.5	25.2 ± 0.1	27.7 ± 1.0	7.4 ± 0.7	7.5 ± 1.7	47.8 ± 5.5	142.5 ± 3.4
MUN6-b	leaf compost (1998)	L	25.1 ± 1.8	23.3 ± 1.7	25.6 ± 2.1	32.8 ± 2.4	10.1 ± 0.4	11.2 ± 0.4	60.4 ± 0.3	167.2 ± 8.3
MUN7-a	leaf compost (1997)	L	15.7 ± 2.5	16.1 ± 2.7	17.9 ± 2.2	23.2 ± 0.1	5.5 ± 1.0	5.6 ± 0.4	32.3 ± 0.4	105.2 ± 7.9
MUN7-b	leaf compost (1998)	L	12.0 ± 2.5	13.0 ± 1.4	13.6 ± 1.2	19.0 ± 4.0	2.4 ± 0.5	2.6 ± 0.9	23.2 ± 0.0	80.8 ± 9.1
MUN7-c	leaf compost (1999)	L	6.0 ± 0.3	6.7 ± 0.3	6.8 ± 0.1	8.0 ± 0.6	1.8#	2.1#	11.7 ± 0.5	39.3 ± 1.6
MUN7-d	topsoil	TS (muni)	2.1#	2.0#	2.5 ± 0.0	3.3 ± 0.3	2.3#	2.8#	4.1 ± 1.2	13.9 ± 0.9
MUN8	leaf compost (1999)	L	42.1 ± 1.2	44.8 ± 1.9	50.9 ± 0.4	59.6 ± 3.5	16.2 ± 0.2	15.7 ± 0.5	87.4 ± 0.3	284.8 ± 4.2
MUN9	leaf compost (2000)	L	58.9 ± 0.5	58.2 ± 3.0	70.2 ± 7.0	79.6 ± 2.2	20.7 ± 1.6	20.6 ± 5.3	148.5 ± 22.4	415.4 ± 14.2
MUN10-a	leaf compost (1998)	L	3.3#	4.8#	5.0 ± 0.8	9.6 ± 0.8	2.3#	3.9 ± 1.3	31.1 ± 0.8	53.5 ± 1.3
MUN10-b	leaf compost (1997)	L	10.5 ± 0.9	11.1 ± 2.1	12.3 ± 0.7	15.7 ± 0.8	4.9 ± 1.0	6.0 ± 0.7	36.9 ± 1.8	86.4 ± 6.3
MUN11-a	leaf compost (1999)	L	21.9 ± 1.3	27.8 ± 1.5	26.9 ± 2.0	36.7 ± 0.8	7.1 ± 0.6	10.6 ± 0.5	68.3 ± 10.9	181.6 ± 16.5
MUN11-b	leaf compost (1999) + double-ground wood chip	L	20.3 ± 0.2	22.4 ± 0.0	21.4 ± 1.1	31.0 ± 0.5	6.4 ± 0.1	7.8 ± 0.5	39.1 ± 1.7	134.1 ± 3.5
MUN11-c	double-ground wood chips	L	14.4 ± 0.5	15.9 ± 0.2	15.4 ± 0.6	16.2 ± 0.6	5.7 ± 0.1	5.5 ± 0.5	28.4 ± 1.0	90.3 ± 1.7
MUN11-d	leaf compost (2000)	L	16.5 ± 0.2	18.3 ± 0.1	20.7 ± 0.7	21.7 ± 1.4	6.4 ± 1.0	5.6 ± 0.6	32.2 ± 2.0	109.4 ± 4.1
MUN11-e	topsoil	TS (muni)	4.0 ± 0.1	3.9 ± 0.3	3.6 ± 0.5	4.4 ± 0.2	1.8#	1.2#	7.3 ± 1.8	23.1 ± 1.0
MUN12-a	leaf compost (1999) with road sweeping (sand)	L + TS	5.3 ± 0.2	5.7 ± 0.6	5.6 ± 0.5	6.5 ± 0.0	1.8#	1.9#	7.3 ± 2.1	30.4 ± 0.8
MUN12-b	leaf compost (2000)	L	15.9 ± 1.4	17.2 ± 0.7	18.9 ± 3.8	21.9 ± 0.5	4.5 ± 0.7	6.2 ± 0.1	30.2 ± 0.8	104.1 ± 3.1
MUN13-a	leaf compost (2000)	L	51.5 ± 0.2	57.8 ± 1.7	69.3 ± 3.2	73.9 ± 3.9	21.5 ± 0.6	24.3 ± 0.5	107.3 ± 0.9	359.7 ± 9.8
MUN13-b	leaf compost (2000) mixed with topsoil (50:50)	L + TS	7.5 ± 0.1	8.3 ± 0.4	10.0 ± 0.7	10.5 ± 1.1	2.6 ± 0.3	3.2 ± 0.4	13.5 ± 0.7	49.7 ± 2.8
MUN14-a	leaf compost (1997, 1998)	L	6.8 ± 0.4	7.5 ± 0.1	8.9 ± 0.5	9.7 ± 0.3	2.6#	3.2#	14.0 ± 0.3	46.9 ± 0.8
MUN14-b	leaf compost (2000)	L	8.0 ± 0.4	8.6 ± 0.5	10.8 ± 0.7	11.4 ± 0.5	3.1 ± 0.5	3.6 ± 0.1	15.1 ± 1.1	53.8 ± 3.2
MUN15-a	leaf compost (1999)	L	14.9 ± 2.3	16.3 ± 2.7	19.5 ± 3.0	21.2 ± 3.3	7.7 ± 1.2	8.6 ± 1.5	39.2 ± 5.3	111.1 ± 16.5
MUN15-b	yard waste compost (1998)	L	38.6 ± 0.5	42.0 ± 0.4	46.2 ± 0.1	48.3 ± 0.4	17.0 ± 0.6	19.2 ± 0.6	79.4 ± 1.7	254.6 ± 1.3
MUN16	leaf compost (screened, 1999)	L	22.6 ± 1.0	23.6 ± 0.5	27.1 ± 0.1	29.8 ± 1.4	9.7 ± 0.9	10.9 ± 0.2	40.6 ± 0.6	143.8 ± 1.1
MUN17-a	leaf compost (unscreened, 1999)	L	5.2 ± 0.2	5.4 ± 0.1	7.0 ± 0.2	7.8 ± 0.2	2.7 ± 0.1	3.6 ± 0.4	13.4 ± 1.0	38.8 ± 1.1
MUN17-b	leaf compost (unscreened, 1998, 1999)	L	4.9 ± 0.4	5.4 ± 1.0	6.6 ± 0.4	7.5 ± 0.5	2.7 ± 0.1	3.2 ± 0.4	14.5 ± 0.4	38.9 ± 2.0
MUN17	leaf compost (unscreened, 2000(?))	L	8.7 ± 1.1	8.6 ± 1.0	8.8 ± 1.5	9.4 ± 1.7	3.0 ± 0.8	3.6 ± 0.5	16.0 ± 0.8	51.4 ± 6.1
MUN18	leaf compost, 1999	L	14.1 ± 1.6	15.1 ± 0.9	18.7 ± 2.0	21.1 ± 1.8	4.8 ± 1.4	6.8 ± 0.3	24.9 ± 1.2	93.8 ± 7.4
MUN19	leaf compost, unscreened 1999	L	27.1 ± 1.4	28.9 ± 1.1	27.2 ± 0.6	36.8 ± 1.5	8.9 ± 1.2	10.4 ± 0.1	85.3 ± 1.8	205.3 ± 3.1

[†] Samples of commercial products (CP) coded with the same number indicate variations within a given brand. Similarly, municipal samples (MUN) from the same site are coded with the same number.

[‡] For commercial samples: C, containing organic and manure compost; TS (comm), containing topsoil and/or sand; C + TS, containing a mixture of compost and topsoil. For municipal samples: L, leaf and/or wood chip compost; TS (muni), primarily topsoil; L + TS, a mixture of leaf compost and topsoil-sand.

[§] TC, *trans*-chlordane; CC, *cis*-chlordane; MC-5, enantiomer of a chiral, minor, but persistent component of the technical mixture; TN, *trans*-nonachlor.

[¶] Values below the limit of detection (LOD).

Approximate concentration, values below the limit of quantitation (LOQ) but above the LOD.

Table 2. Comparison of chlordane concentration in composts.

Location (reference)	Year of analysis	Number of samples	Total chlordane concentration		
			Average	Standard deviation	Highest concentration reported
			$\mu\text{g/kg}$		
Connecticut (present work) [†]	2001	33	127	91	415
New Jersey (Strom, 2000)	1993	12	1070	919	3230
New York (Richard and Chadsey, 1990)	1989	12	93	119	—
Oregon (Heberg et al., 1991)	1988–1989	19	187	—	370
Illinois (Miller et al., 1992)	1991	43	400	284	1380

[†] Includes only samples of leaf compost.

to deduce the magnitude of the contribution of compost to the cycling of chlordane through the biosphere. The first approach is a measure of the total chlordane in product produced annually by a compost facility. For this calculation the total chlordane concentrations in the finished leaf composts, L, shown in Table 1 were employed, together with the capacity in cubic yards of each facility sampled, and the reduction factor of 100 to 200 yd³ (76 to 153 m³) of finished leaf compost for every 10³ yd³ (7646 m³) of leaf feedstock (Connecticut Department of Environmental Protection, 2002), and typical moisture content in compost of 45 to 50%. On this basis total chlordane leaving the facilities examined in this work ranged from a low of 4.5 up to 412 g/yr. Higher chlordane concentrations in the finished compost, as reported in the studies summarized in Table 2, together with a larger total volume of finished product from larger municipal compost facilities, will result obviously in more substantial translocation of chlordane through the environment than the amounts reported here. The values demonstrate that anthropogenic translocation via compost of at least one POP, chlordane,

cannot be ignored in assessing total POP cycling through the biosphere.

A second calculation predicts the resulting chlordane concentration in soil amended with the most contaminated leaf compost in this study, one containing 400 $\mu\text{g/kg}$ chlordane on a dry weight basis, which is at the low end of the range of contamination reported in Table 2 as mentioned previously. For this calculation an application rate of 370 m³/ha (or 4.5 yd³/1000 ft²) was assumed, an amount at the mid-point of the recommended range (United States Composting Council, 2000). Using these values we calculate that 18 g chlordane will be amended into one acre. Assuming that the original chlordane concentration on this one acre of land is zero, and that the compost is amended solely into the top 7.6 cm of soil, a final concentration of 44.5 $\mu\text{g/kg}$ will result. In performing this calculation we have assumed a soil weight of 6×10^4 kg/cm acre (6×10^4 kg/cm 4047 m²) (Brady and Weil, 1999, p. 138) and a soil moisture content of 10 to 20% as observed in this laboratory. Since there are no reports regarding the fate of chlordane in compost-amended soil, such as degradation, plant uptake, and volatilization, this calculation alone indicates that compost amendments over several seasons may produce a significant cumulative chlordane concentration in field soils. Once again, the value demonstrates that anthropogenic translocation via compost of at least one POP, chlordane, cannot be ignored in assessing total POP cycling through the biosphere.

These two calculations of the magnitude of a point-source contribution (from compost) may be compared with that of a nonpoint-source contribution to assess the cycling of chlordane through the biosphere. Based on flux measurements of chlordane from a well-characterized, weathered, chlordane-contaminated site, Eitzer has calculated that 2.4% of the weathered residue will volatilize from the soil annually (Eitzer, unpublished data, 2001). Based on this flux for the average agricultural

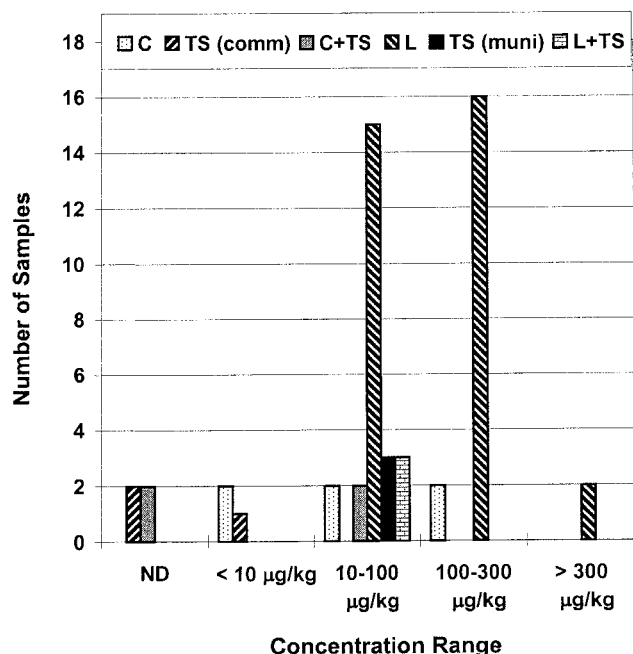


Fig. 1. Distribution of chlordane in compost samples. C, containing organic and manure compost; TS (comm), containing topsoil and/or sand; C + TS, containing a mixture of compost and topsoil; L, leaf and/or wood chip compost; TS (muni), primarily topsoil; L + TS, a mixture of leaf compost and topsoil-sand.

Table 3. Chlordane concentrations from leaf and soil[†] samples.

Description, collection date	Leaf	Soil
White oak [‡] , June 2001	ND§	168
White oak, September 2001	5.0	
White oak [‡] , June 2001	ND	324
White oak, September 2001	6.6	
Hickory, September 2001	1.2	960
Maple, November 2001	6.2	97
Oak, December 2001	8.1	215
Chestnut, December 2001	10.5	6.5

[†] All soil samples are composites from within the drip line of the tree.

[‡] Two different trees at two different locations.

§ Not determined.

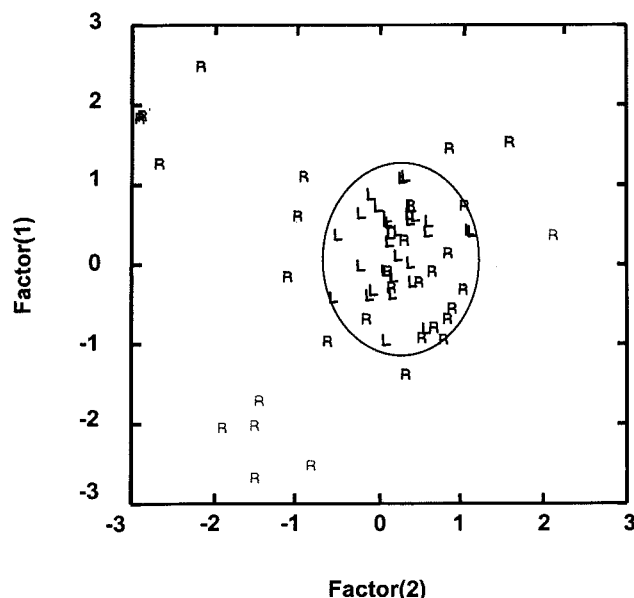


Fig. 2. Principal component analysis of normalized data set for leaf composts and residential soil samples.

field in Connecticut having a weathered concentration of 140 μg chlordane/kg dry soil (Incorvia Mattina et al., 1999), we compute that 1.4 g chlordane/acre (1.4 g chlordane/4047 m^2) will volatilize from this soil annually. If this output value is compared with the input value, 18 g, from the above calculations, there is no question that contributions from the point source, compost, must be taken into account, together with nonpoint sources, such as volatilization from soil, to develop a comprehensive assessment of chlordane cycling through the biosphere.

Compositional and Enantiomeric Profiles of Chlordane Residues

Enantiomer fractions (EFs) of (+)-TC and (+)-CC in commercial products and municipal composts were determined as defined in Eq. [1]:

$$C(+)/[C(+) + C(-)] = \text{EF} \quad [1]$$

where $C(+)$ and $C(-)$ are the concentrations of (+) and (−) enantiomers, respectively. Using chiral gas chromatography interfaced to ion trap mass spectrometry we have measured EFs equal to 0.50 ± 0.01 for both TC and CC in solutions of the standards, representing the racemic condition on the instrumentation in our laboratories. The racemic condition also pertains at the time of original application of technical chlordane. Examination of EF values of chiral compounds in different matrices provides insight into their fate in the environment. Physical properties, for example, volatility and solubility, which are the primary factors affecting the fate of the residues under abiotic conditions, do not discriminate between enantiomers. In contrast, degradation of chiral pesticides due to biotic interactions is usually enantioselective (Ulrich and Hites, 1998), producing nonracemic residues and an alteration of the original EFs. The EF values in compost samples from this study ranged from 0.45 to 0.52 for (+)-TC and 0.51

Table 4. Parameters from the principal component analysis.

Parameter [†]	Factor 1	Factor 2
+TC component loading	0.694	0.694
−TC component loading	0.745	0.635
−CC component loading	0.818	−0.514
+CC component loading	0.708	−0.667
TN component loading	−0.998	0.061
Percent of total variance	64	32

[†] TC, *trans*-chlordane; CC, *cis*-chlordane; TN, *trans*-nonachlor.

to 0.58 for (+)-CC. Eitzer et al. (2001) have examined the EF profiles of chlordane components in soil, and reported a similar preference for more rapid loss of the (+)-TC and (−)-CC enantiomers. Based on reported insect LD_{50} values for the enantiomers (Incorvia Mattina et al., 2002), the selective accumulation of (−)-TC will render the chlordane residues more toxic, while preferential accumulation of (+)-CC makes them less toxic, relative to a comparable racemic concentration.

It is informative to pursue comparisons of the chlordane profiles in soil and leaf compost. Such profiles refer to both compositional profiles, as described by the concentration of the +TC, −TC, +CC, −CC, and TN components, each normalized to the total chlordane concentration within a compartment, as well as the enantiomeric profiles, as described by the EF (+TC) and EF (+CC) values. For the comparisons the selected soil samples (designated R in Fig. 2) have been limited to 32 samples from Connecticut residential lawns and gardens as previously reported (Incorvia Mattina et al., 1999; Eitzer et al., 2001); the 32 compost samples (designated L in Fig. 2) have been limited to municipal leaf composting facilities in Connecticut. These samples constitute the most logical comparison of data accumulated to date, the assumption being that feedstock for municipal leaf composting facilities will be collected from residential lawns and gardens with potential contamination by soil from these locations. For principal component analysis (PCA) the concentrations of +TC, −TC, +CC, −CC, and TN for each sample were normalized to the sum of these five components in each sample; the normalized data set was then subjected to PCA. The Factor (1) versus Factor (2) plot is shown in Fig. 2; the oval enclosing L symbols is intended solely to emphasize the clustering of the Ls in this figure. Component loadings and percent variance from the PCA are provided in Table 4. The component loadings indicate that Factor (1), which accounts for 64% of the variance, is driven primarily by the absolute and directional orientation of TN values compared with TC and CC values. The component loadings indicate that Factor (2) is driven primarily by different directional orientations between TC and CC values, with TN values having minimal effect.

The second comparison of the 32 R samples with the 32 L samples, shown in the plot of EF (+TC) versus EF (+CC) of Fig. 3, attempts to ascertain if enantiomer profiles correlate differently in the R and L samples. The full data set, EF (+TC) for L, EF (+TC) for R, EF (+CC) for L, and EF (+CC) for R, was analyzed by means of the Pearson Product Moment Correlation. While there is scatter in both the L and R samples,

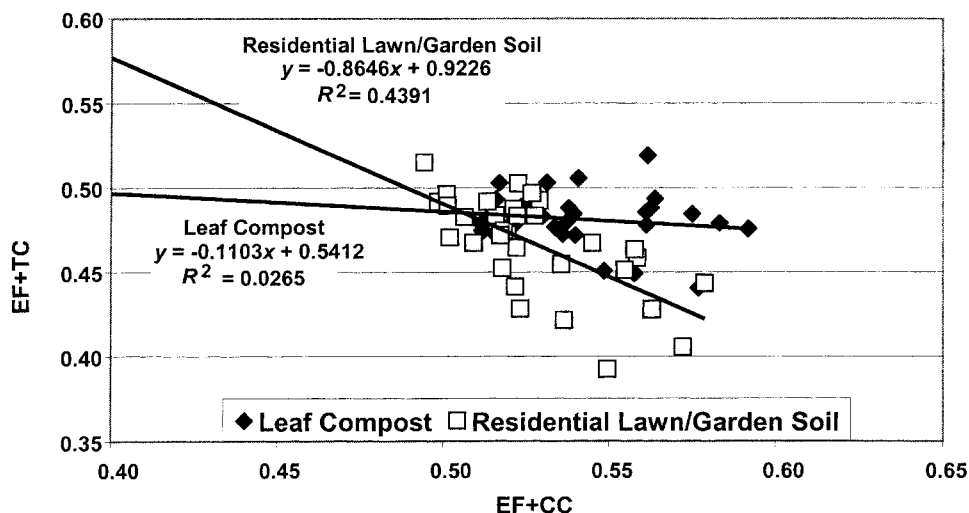


Fig. 3. Correlation of enantiomer fraction (EF) + *trans*-chlordane (TC) with EF + *cis*-chlordane (CC) for leaf composts and residential soil samples.

the EF (+TC) and EF (+CC) for the R samples are significantly correlated, $P < 0.05$ (coefficient of correlation equal to -0.66); the EF (+TC) and EF (+CC) for the L samples are not significantly correlated, $P > 0.05$ (coefficient of correlation equal to -0.16). From this analysis we can conclude that the 32 L samples were drawn from a different population than the 32 R samples.

Based on both the PCA and correlation analyses of the data to date, the finished leaf compost represents a matrix *different* from soil, rather than one merely diluted with soil. Unequivocal confirmation of this conclusion requires that the chlordane residues be tracked through the composting process from feedstock to finished product. These studies are being planned.

CONCLUSIONS

This study establishes that a wide variety of compost products contain chlordane residues. Based on concentrations and quantity of leaf compost produced, the data indicate that leaf compost contributes to the anthropogenic translocation of at least one POP, chlordane.

There is strong evidence from the data that soil is not the sole feedstock source of chlordane; vegetative matter such as leaves, grass clippings, and yard waste is also a likely contributor of chlordane to the final product. Although the highest chlordane concentration, $415.4 \mu\text{g/kg}$, observed in a municipal leaf compost sample (MUN9) from this study, is lower than the USEPA soil screening level (SSL) of $500 \mu\text{g/kg}$ (USEPA, 1996), the validity of assuming that a chlordane concentration in soil is equivalent to the same concentration in compost is questionable. Sequestration of contaminants in soils is associated with decreased bioavailability or biodegradability due to partitioning of the contaminants into soil organic matter (Hatzinger and Alexander, 1995) and/or the nanoporous soil structure (Alexander, 2000). Due to this partitioning over time, weathered POPs in soil have been assumed to have very low extractability and bioavailability to a range of receptors (bacteria, earthworms, insects). However, from our earlier studies

it is known that certain plants, for example, zucchini and pumpkin, uptake and accumulate significant amounts of POPs (for example, chlordane and *p,p'*-DDE) from soil containing the weathered residues (White, 2001; Incorvia Mattina et al., 2002; White et al., 2002). This observation has led to an intensive investigation in our laboratory of the precise mechanisms involved in the uptake of POPs from soil. Differences among soils, as well as microbial populations within the soil, can affect bioavailability and biodegradability of sequestered compounds, and the concomitant enantioselectivity of these processes on chiral sequestered compounds (Lewis et al., 1999). The data presented in Fig. 2 and 3 underscore differences between the two matrices of soil and a vegetation-based leaf compost. In addition, compost lacks the nanoporous sequestering structure typical of soil and its higher organic matter content is expected to produce an increase of microbial activity. Therefore, it is likely that the bioavailability to flora of POPs in compost is markedly different from that of comparable soil concentrations. Since no data is available at present to assess the bioavailability of POPs from the compost matrix, the suitability of applying soil contaminant guidelines to compost is questionable.

The pathways for contamination of vegetative feedstocks by POPs have not been extensively explored in this report. While uptake of chlordane by plants from weathered soil residues is mentioned in the Results and Discussion section, a second pathway of contamination is that of an air-to-plant route. This route has been proposed in the literature (Hülster et al., 1994; Nakagawa et al., 2002) and is implicit in the data in Table 3. Once again considerably more research is necessary to establish what contribution this route makes to the chlordane concentration in the finished product.

All the issues enumerated here must be addressed to elucidate the full effect of compost use on human health as well as its comprehensive contribution to the cycling of POPs through the biosphere.

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